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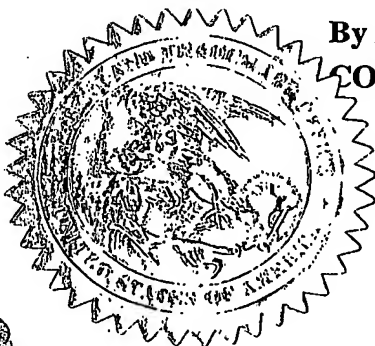
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**APPLICATION NUMBER: 60/439,811**

**FILING DATE: January 14, 2003**

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## PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(b)(2)

Docket Number		11439-1		Type a Plus Sign (+) inside this Box -->		+	
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TITLE OF THE INVENTION (280 CHARACTERS MAX.)							
Crosslinkable Functional Materials Based Upon Organoboronic Acids or Organoboronates For Multi-layer Devices							
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STATE		Ontario		ZIP CODE		K1A 0R6 COUNTRY Canada	
ENCLOSED APPLICATION PARTS (Check all that Apply)							
X	Specification	Number of pages	33	Small Entity Statement			
X	Drawing(s)	Number of Sheets		Other (specify)			
METHOD OF PAYMENT (Check One)							
	A check or money order is enclosed to cover the Provisional filing fees					Provisional Filing Fee Amount (\$)	\$ 160.00
X	The Commissioner is hereby authorized to charge filing fees and any deficiency in the filing fees and credit to our <u>Mastercard Account</u> Form PTO-2038 is attached						
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The invention was made by an agency of the United States Government or under contract with an agency of the United States Government.

☒ No

Date: January 14, 2003

Respectfully submitted,

:ech

J. Wayne Anderson  
Patent Agent for Applicant  
Regn No. 28,158

Enclosures

☒ Additional inventors are being named a separately numbered sheets attached hereto.

/14/03 18:36 6139988333

BUSINESS RELATIONS

60439811.1

PROVISIONAL APPLICATION FILING ONLY

Docket Number		11439-1		Type a Plus Sign (+) inside this Box ->	+
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January 7, 2003

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BY FAX: 1-703-415-2520

To the attention of Ms. Janice L. NICHOLS  
President

Re : PCT application PCT/US98/02618  
Claiming priorities of US 60/037.605  
US 09/015.565  
O/Ref.: LAVOIX 003810-9998

Dear Madam:

Our client is interested in having complete copies of the two (2) US applications,  
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The concerned US applications are:

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Crosslinkable functional materials based upon organoboronic acids or organoboronates for multi-layer devices.

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## BACKGROUND OF THE INVENTION

Many *organic or polymeric* optic, electronic and optoelectronic devices, such as light-emitting diodes (LEDs), field-effect transistors (FETs), solar cells, optical waveguides, etc., require high quality organic multi-layered configurations to optimise their performance.<sup>1-3</sup>

In the fabrication of organic or polymeric light emitting devices it is advantageous to incorporate multi-layered structured materials with special functions into different location within the device. For instance, organic or polymer light-emitting diodes (LEDs) with a stack of hole-transporting, electron-transporting, and light-emitting layers exhibit enhanced device efficiency, higher brightness, and better stability. Solvent-based or wet-processing techniques such as reel-to-reel printing, screen-printing or spin-coating are important fabrication techniques that could significantly reduce fabrication costs of organic/polymer devices. However, the fabrication of multi-layer device structure is often difficult with wet-processing techniques. One typical problem of making multi-layered structures using solutions is the fact that the solvent used for each successive layers can lead to swelling or dissolution of underlying layers.

In addition, in the case of some polymeric materials, it has been found when they are used in applications such as light-emitting diodes aggregation and excimer formation can occur which can cause poor optical stability in the fabricated devices.<sup>4</sup> For example, upon heating, or on passage of an electrical current through a polyfluorene based polymer, the formation of a long wavelength emission is frequently observed in the region 500 – 600 nm which can cause a drastic drop in the emission efficiency.<sup>5</sup>

(A) Multi-layer devices, are currently being fabricated using the following methods:

- i) For low molecular weight organic materials, vacuum deposition is usually used for making a multi-layered device structure.
- ii) Since a multi-layered device structure is advantageous in highly efficient polymer based devices, much research effort has been devoted to this area. Researchers have developed different strategies to fabricate multi-layered PLED structures using 1) polymer materials with very different solubilities for the different layers in a multi-layered structure, 2) plastic lamination processes or cross-linkable polymer layers, as well as 3) chemical vapor deposition to avoid the use of solvents. Bernius et al.<sup>6</sup> reported the use of fluorene triphenylamine copolymers with carboxylic acid substituents for the hole-transport layer, as these are soluble in polar solvents like DMF, but practically insoluble in aromatic hydrocarbons such as toluene and xylene. An electron-transport and emitting fluorene polymer layer was then spin-coated on top of this layer using a xylene solution. A double layer structure with sharp polymer-polymer interface was successfully produced using this method. Hay et al. have developed

5 a new series of arylamine-based hole-transport polymer<sup>7,8</sup> that can only  
be dissolved in some organic solvents such as chloroform, for use in the  
fabrication of double layer PLEDs. By using electron transporting  
10 polymers that are soluble in toluene, double layered polymer blue light  
emitting devices have been successfully fabricated<sup>9</sup>. Yang and his co-  
workers<sup>10</sup> recently reported a low temperature lamination method using a  
'template activated surface process' to fabricate high performance double  
15 layer blue and red-emitting PLEDs at a temperatures much lower than the  
 $T_g$  of the polymers used in their devices. The discovery of cross-linkable  
oligo- and poly(dialkylfluorene)s series<sup>11-13</sup> certainly opened the door for  
multi-layer PLED fabrication using solution processable and thermally  
cross-linkable polymeric or oligomeric materials. As an alternative  
20 approach for making multi-layered polymer devices, Murata<sup>14</sup> recently  
reported a two-layered polymer light emitting device prepared by a vapor  
deposition polymerization process, which has the advantage of using a  
solvent-free fabrication environment to produce a good thin film with  
consistency in uniformity, and minimum contamination. Unfortunately the  
fabrication costs associated with this process are a problem. In addition it  
the vapor phase polycondensation reaction used in this process may be  
difficult to apply to other polymer systems.

25 (B) In terms of the problems associated with aggregation and excimer formation,  
several approaches<sup>16-18</sup> have been proposed to stabilise the optical properties of  
polymers used in light-emitting materials. These include:

- 30 i) Incorporation of bulky substituents into the polymer backbone or at the  
chain ends to enlarge the intermolecular distance.  
ii) Copolymerization with other monomers to hamper chain alignment.  
iii) Introduction of spiro-structures to decrease the crystallization tendency.  
iv) Thermal-crosslinking of precursor oligomers via styryl chain end groups to  
form amorphous networks.

35 Although the vacuum deposition is a very good technique for the fabrication of multi-  
layered device structure, it is limited to low molecular weight organic materials and  
because of the use of a high vacuum system, the production costs will be higher than  
using solvent-based wet processing techniques. Another possible disadvantage is that  
crystallization of the organic thin films may occur upon heating or operation, which could  
cause device failure.

40 The use of crosslinkable polymeric materials meanwhile through spin-coating, solution-  
casting, or dip-coating requires the attachment of crosslinkable functionalities to the  
polymers. This can complicate the synthetic procedure and needs to be optimised in  
terms of crosslink content and crosslinking conditions. In addition, in many cases thermal  
or photo initiators are necessary for the crosslinking reactions to occur. These initiators  
45 can give rise to very reactive radicals, which have the potential of altering the materials'  
chemical structure, which can result in defects, which may be detrimental to the device's

performance and lifetime. In addition the presence of initiator residues can contaminate the materials.

5 From a chemical structural point of view it should also be noted that while the approaches listed in section (B) i), ii), and iii) may result in some improvements in the optical stability, these techniques have so far not resulted in the complete suppression of aggregation. On the other hand while an approach such as (B), iv) could be used to obtain materials with good colour stability, the method does require a relatively high processing temperature (~200 °C) to initiate the crosslinking reaction. In addition, because the reaction involves 10 the formation of very reactive radicals, changes to the polymer backbone are possible which can result in structural defects that are detrimental to the materials' stability and influence other components (e.g., charge-transporting layers).

15 It is also known that organoboronic acids undergo self-condensation (dehydration) reactions under vacuum or/and heating to form trialkyl-(or triaryl-) boroxine structures.<sup>4,6</sup> Therefore, the use of di- or multi-organoboronic acids, can lead to the formation of cross-linked networks.<sup>6</sup>

## 20 SUMMARY OF THE INVENTION

25 According to one aspect of the invention a method is provided for the esterification of boronic acids and the transesterification of boronates with alcohols or thiols to form a cross-linkable functional material intermediate, that can readily be cross-linked e.g. by heating, to form multi-layer (light-emitting layers and charge-transporting layers) useful for the production of various electronic components e.g. light-emitting diodes (LEDs), and other electronic and optoelectronic devices.

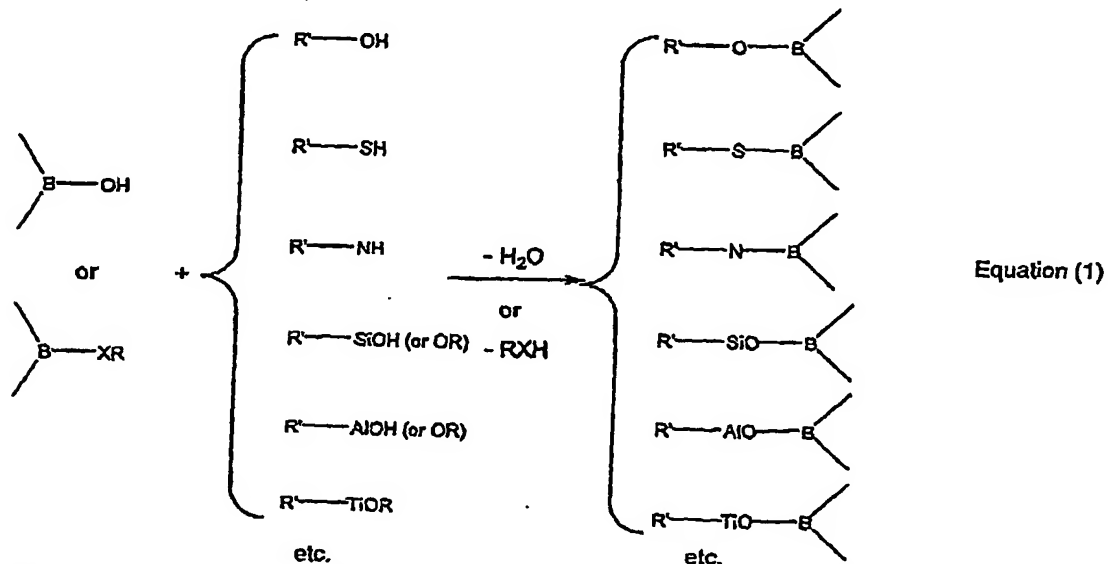
30 According to another aspect of the invention, if the organic moiety of the boronic acid is a functional group, such as, an electron-withdrawing, electron-donating, or light-emitting group, then the resulting network materials could be used as charge-transporting or light-emitting layers in LED's or other electronic or optoelectronic devices.

35 In addition to using boronic acids as outlined above, it is also possible to react boronic acids or boronates with di- or polyalcohols (or thiols) to form cross-linkable intermediates e.g. thin films, which may be crosslinked e.g. by heating, to form networks for use in a wide range of optical devices such as of light-emitting diodes (LEDs) for example. Boronic acids react with simple alcohols, diols, and polyols under 40 mild reaction conditions to form covalent esters.<sup>21-23</sup> When a boronic acid reacts with a polyol, or a boronic acid possessing di- or multiple boronic acid groups with a diol or polyol, a cross-linked network material can be expected (see Figure 1), and Scheme 1 and 2). Dithiols or polythiols can also be used instead of the alcohols.

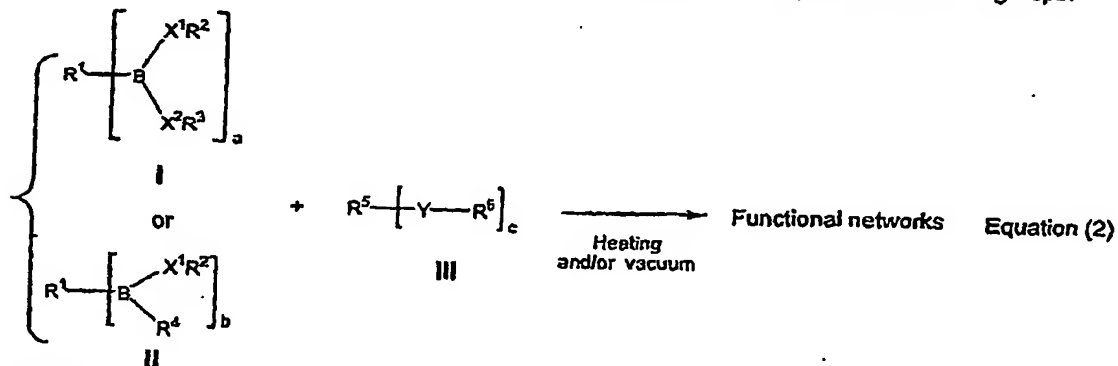
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Similarly, the transesterification of boronates with alcohols or thiols readily occurs on heating. If a non-volatile diol or polyol is used for the reaction the resulting small molecule alcohol produced can be readily removed from the system, to give an immobilized cross-linked structure due to the formation of the new ester linkages (Scheme 3).



wherein, X = O, S, N; R and R' = alkyl, aryl, or any other organic and inorganic structures or groups.



wherein,

R<sup>1</sup>, R<sup>4</sup>, and R<sup>5</sup> = alkyl, aryl, or other groups, either organic or inorganic, but at least one of them contains functionality; they can be of small molecular weights or high molecular weights.

R<sup>2</sup>, R<sup>3</sup>, R<sup>6</sup> = H, alkyl, aryl, they may be same or different, but at least one of them is H.

X<sup>1</sup>, X<sup>2</sup> = O, S, or N, they may be same or different.

Y = O, S, N (or NH), SiO, AlO, TiO, etc.

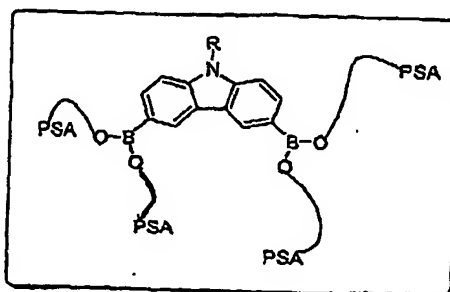
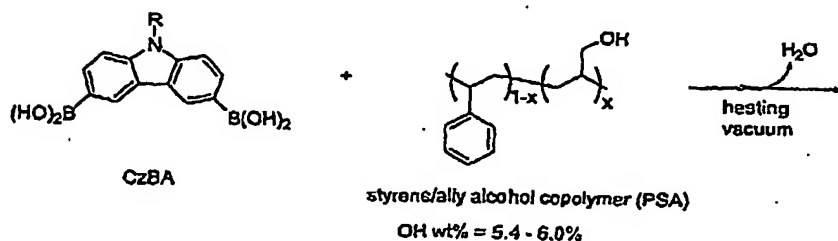
a, b, c are equal to or larger than one, but at least either a (or b) or c is larger than one.

Figure 1. Cross-linking reactions of boronic acids or boronates with other components.

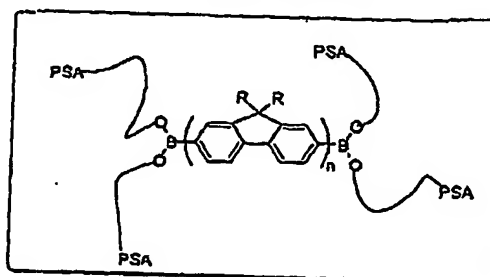
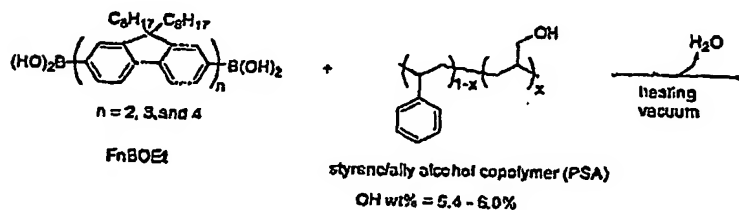


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Scheme 1. Formation of hole-transporting networks via esterification of CzBA with PSA.

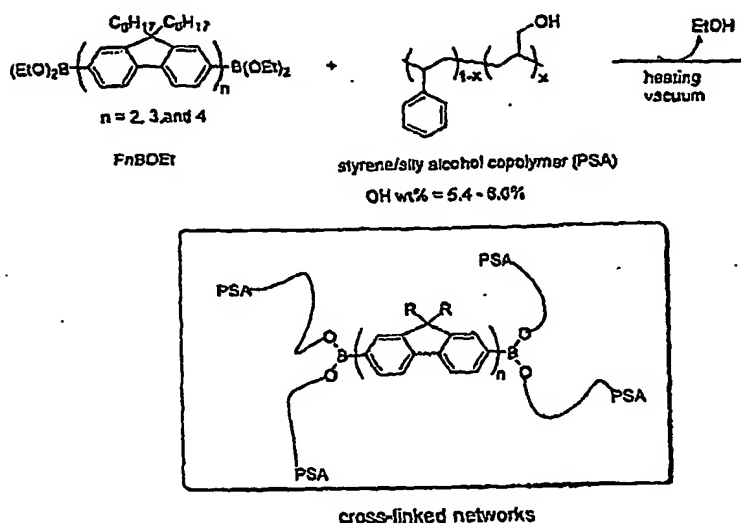


Scheme 2. Formation of blue-light emitting networks via esterification of FBA with PSA.



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Scheme 3. Formation of blue-light emitting networks via transesterification of FnBOEt with PSA.



The novel crosslinked networks containing light emitting moieties have the potential of resolving problems associated with chain aggregation and/or excimer formation that can occur in LED's.

The crosslinkable components containing CzBA/PSA, FnBA/PSA, and FnBOEt/PSA have been used to form crosslinked hole-transporting and light-emitting thin films to demonstrate the feasibility of this approach (Scheme 1 - 3).

The organoboronic acids, CzBA, FnBA, and poly(styrene-co-allyl alcohol) (PSA) are readily soluble in THF. The THF solutions of CzBA/PSA, FnBA/PSA, and FnBOEt/PSA can be used to fabricate thin films using traditional approaches such as spin-coating, solution-casting, or dip-coating techniques. Once the film has been prepared it can be crosslinked using mild reaction conditions (e.g., 120 °C, 2h) in which water is the by-product, that can be removed by vacuum (this reaction has been confirmed by FT-IR analysis). This thermal treatment procedure produces crosslinked thin films that are insoluble in water alone or in any anhydrous organic solvents. These films are also resistant to most wet common solvents such as THF and acetone. The crosslinked films produced as outlined above have higher optical stabilities (UV absorption and fluorescence) at elevated temperatures (e.g., 120 °C, 24 h) than the crosslinked structures made solely from boronic acids (see Appendix I).

Crosslinked films of CzBA and F3BA have been used as the hole-transporting layer and a blue light-emitting layer, respectively, in a LED device (see Appendix II). Preliminary results demonstrated that (i) the fabrication of a double-layer LED device could be accomplished relatively easily, and (ii) the color stability achieved using these thermally crosslinkable boronic acids are much improved.

It will be appreciated by those skilled in the art that this invention can also be extended to include other functionalities such as amines, silanols (or silicates), aluminum hydroxides (or aluminates), titanium alcoholates, and other metal hydroxide (or alcoholates), that can also be reacted with boronic acids or boronates to form crosslinked networks (Figure 1).

The invention provides the following advantages:

- i) The use of mild crosslinking reaction conditions means that the generation of harmful structural defects is minimised.
- ii) Well-defined structures with identical chromophores, are obtained which give correspondingly sharper emission bands.
- iii) The resulting materials are amorphous on crosslinking and have high glass transition temperatures.
- iv) Both systems effectively suppress chain aggregation and/or excimer formation and result in devices with high stable performance.
- v) Versatility in tuning opto-electronic properties by simply mixing different functional molecules in one solution for the film coating.
- vi) Versatility in structural design to fine-tune the opto-electronic properties.
- vii) High solvent-resistance of the crosslinked structure allows the fabrication of multi-layered devices.
- viii) High purity and mono-disperse chromophores give uniform optical and electronic properties and prevent the defects in the devices. Our experiments(see below) on thin film and device processing show that the thin films are quite uniform as indicated by the uniform thickness interference pattern, and uniform light emission area, which depends strongly on the layer thickness.
- ix) No active, unstable terminal groups as in other crosslinkable polymers, which could detract from the devices' stability.
- x) Thermally stable (organic/inorganic hybrid materials) as indicated in Appendix II by comparing the photoluminescent spectrum and intensity before and after a thermal treatment in vacuum at 130 °C for two hours.
- xi) Multi-layered device structure can be easily realized using materials containing organoboronic acid groups. In Appendix II, we have demonstrated that a CzBA layer and an F<sub>3</sub>BA layer can be stacked on each other forming double layer structure, the total thickness of the double layer structure equals to the sum of the two individual layers. In Appendix III, we demonstrated that we have incorporated desired hole-transporting, electron-transporting and emissive properties into double layer devices using CzBA and F<sub>4</sub>BA, and each layer functioned as designed.
- xii) Because each layer is cross-linked before applying the next layer, this technique can be applied to multi-layer structure or "super-lattice" type structure, not like the solubility based technique that only allows very limited layers.
- xiii) Because organic light emitting devices are very sensitive to the charge mobility, HOMO-LUMO level positions, and interface quality, the demonstration of - working OLED devices using boronic acids or boronates indicates a reasonably

good interface structure between the -hole-transporting layer and the emitting layer. Since OLEDs are only used here as a testing vehicle, we expect the same film processing technique (using organoboronic acid groups as end caps) can be applied to the fabrication of photovoltaic cells, wave guide structures, 1-D photonic crystals using multi-layer structures, and any other electronic or optoelectronic devices using multiplayer structures.

xiv) The properties of each layer are easily tunable by varying functional unit in the monomer or by incorporating different monomers by simply mixing. There are very wide selections of functional units for the monomers with different optical and physical properties. On the other hand, the crosslinking of boronic acid groups enhanced compatibility of different mixed monomers in the layer, and therefore promoted some properties.

xv) Because of crosslinking of the monomers, the amorphous morphology of the layers has been stabilized. The structure with such high crosslinking density will efficiently prevent any aggregation and crystallization, which is usually found in PLED and OLED devices, and cause the performance of the device to decrease. Thus polymer thin films made from this class of materials are not only applicable to multiplayer structures, but can also be used in single layer devices to improve stability, and reduce the possibility of aggregation.

9. These materials can also be used as a matrix to incorporate other functional materials (either small molecules or polymers) such as charge transporters, dyes, etc.

## DETAILED DESCRIPTION OF THE INVENTION

### Appendix I:

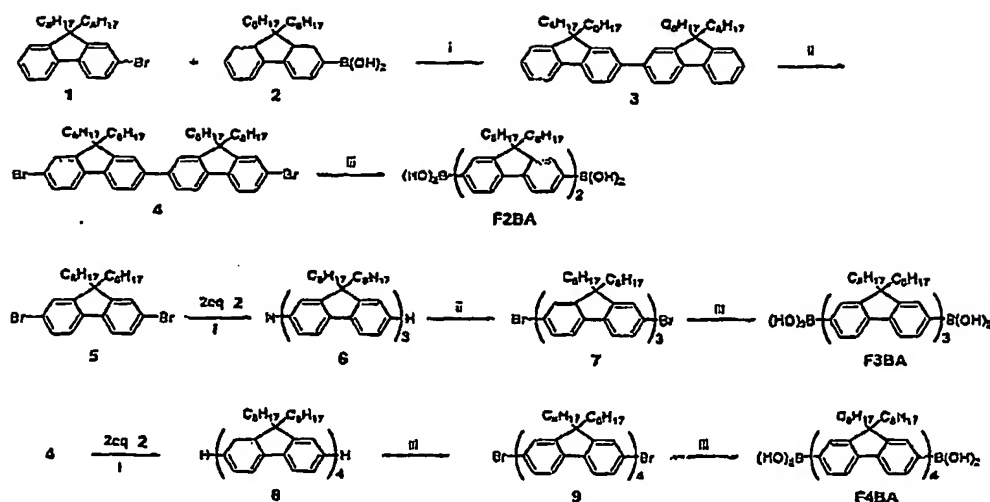
#### Crosslinkable functional materials based upon organoboronic acids or organoboronates for multi-layer devices

### Results and Discussion

#### *1. Self-condensation of oligofluorene diboronic acids to form amorphous polymer networks useful as blue light emitters.*

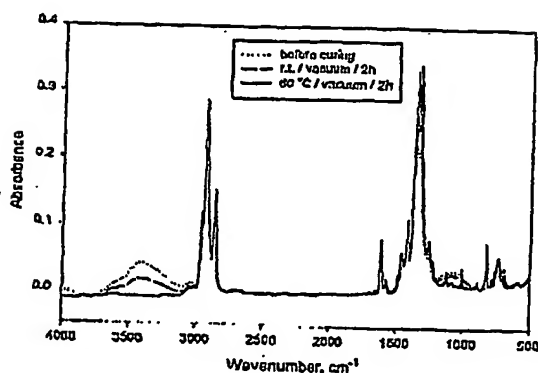
Scheme 1. Syntheses of the oligofluorene diboronic acids.

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i). 2% mol Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M Na<sub>2</sub>CO<sub>3</sub>, toluene, reflux.ii). Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 - r.t.iii). (a) 2.0eq n-BuLi, THF, -78 °C; (b) 4.2 eq B(OiPr)<sub>3</sub>, -78 °C; (c) 2N HCl.

**Materials synthesis.** Oligofluorenes carrying boronic acid groups at 2- and 7-positions, F2BA, F3BA, and F4BA, were synthesized according to procedures outlined in Scheme 1. The starting materials, 2-bromo-9,9-dioctylfluorene (1), 2-dihydroxyboranyl-9,9-dioctylfluorene (2), and 2,7-dibromo-9,9-dioctylfluorene (5), were prepared according to the reported methods. The Suzuki coupling reaction of 1 and 2 was carried out in a refluxing toluene/aqueous 2M Na<sub>2</sub>CO<sub>3</sub> solution containing 2 % mol of Pd(PPh<sub>3</sub>)<sub>4</sub> for 48 h to give the fluorene dimer 3. Bromination of 3 using Br<sub>2</sub> in dichloromethane afforded the dibromo dimer 4. F2BA was then prepared *via* lithiation of 4 using 2.5M *n*-BuLi at -78 °C in THF, followed by subsequent *in-situ* reaction with triisopropylboronate, and hydrolysis with 2N HCl. Similar procedures were used to prepare the diboronic acids F3BA and F4BA from compounds 5 and 4, respectively, as illustrated in Scheme 1. After being dried under vacuum at room temperature, the compounds F2BA, F3BA, and F4BA were reluctant to dissolve in dry solvents, presumably due to the formation of some crosslinked structures through partial dehydration of boronic acid groups (confirmed by the IR spectroscopy). However, when small traces of water were added, they readily dissolved in solvents such as THF, acetone, and DMF. In the presence of water it would appear that the crosslinked linkages in these materials are probably hydrolyzed to release soluble free boronic acids. The resultant solubility of these compounds under these conditions facilitates the characterization of their chemical structures in addition to their fabrication into films by solution casting. The IR spectra of these diboronic acids (the spectrum of F2BA is shown in Figure 1 as an example) clearly revealed the existence of B(OH)<sub>2</sub> groups, which was evidenced by a broad band at 3430 cm<sup>-1</sup> due to the BO - H stretching and a strong absorption around 1330 - 1340 cm<sup>-1</sup> attributable to the asymmetric B-O stretching. <sup>1</sup>H NMR spectra of F2BA and F3BA have also been obtained in acetone-*d*<sub>6</sub> in the presence of trace of D<sub>2</sub>O, which confirm the existence of this structure. Although F4BA could be dissolved in wet acetone, the resultant transparent solution was found to be metastable and became cloudy within minutes, and eventually a white solid precipitated. When an equivalent amount of toluene was added to the mixture, however, the solid dissolved again. The <sup>1</sup>H NMR measurement of F4BA was therefore carried out in a solvent

5 mixture containing toluene- $d_7$ /acetone- $d_6$ /D<sub>2</sub>O (v/v: 20/5/1). The above observed solubility changes noted for F4BA suggest that the intermolecular interactions within F4BA in the solid state are dominated by the hydrogen bonding between boronic acid groups. Once the hydrogen bonding has been destroyed by the polar solvents, the hydrophobic moieties in F4BA self-assemble to aggregates, which is driven by the intermolecular van der Waals force. As will be discussed below, this strong hydrogen bonding presumably has the effect of overcoming the weaker intermolecular  $\pi$ - $\pi$  interaction, thereby completely suppressing chain aggregation and/or excimer formation in the solid state.

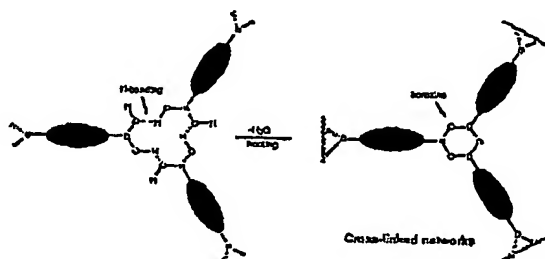


10 Figure 1. IR spectra of F2BA.

**Cross-linking reaction.** Polymer films on KBr disks were prepared by casting solutions of F2BA, F3BA, and F4BA in THF followed by the evaporation of the solvent in the air. These films were subjected to IR measurements. The cast films were then cross-linked in a vacuum oven at  
15 different temperatures. As shown in Figure 1, the IR absorption of the BO-H groups of F2BA at 1331 cm<sup>-1</sup> virtually disappear after heating at 60 °C for 2 h. At the same time a new absorption peak at 732 cm<sup>-1</sup>, assigned to the out-of-plane vibration of the boroxine structure appears. Similar IR results were observed for F3BA and F4BA (spectra not shown). These changes in the IR  
20 spectra strongly suggest the formation of cross-linked networks *via* the formation of six-membered boroxine rings (Scheme 2). It was also noted that this dehydration could also occur at room temperature (Figure 1). The ease of this dehydration reaction in the solid state under such mild reactions  
25 conditions might be accounted for the close proximity of boronic acid groups to each other due to hydrogen bonding (Scheme 2). As mentioned above, these cross-linked structures can be readily hydrolysed in the presence of wet

polar solvents such as THF and acetone, but they are insoluble in water alone and in anhydrous organic solvents. This property offers excellent processing capabilities for the materials, facilitating the fabrication of multi-layered films by the use of anhydrous solvents. This property should also pose no problem for these materials in applications requiring a dry atmosphere such as LEDs.

Scheme 2



**Thermal properties.** DSC and TGA analyses were performed on the F2BA, F3BA, and F4BA sample as prepared. The DSC curve of the F2BA on the first heating scan (r. t. ~ 250 °C) shows a large endothermic peak at 125 °C (Figure 2), associated with the melting and partially dehydration of the boronic acid groups (confirmed by TGA analysis). Similarly the F3BA and F4BA samples exhibited broad melting points that peaked at 86 and 63 °C, respectively. However it was interesting to note that their heat capacities were much lower than that of F2BA, suggesting that these materials have low degrees of crystallinity. On the other hand, after being cured at 110 °C under vacuum for 2 h, the F2BA, F3BA, and F4BA samples showed no melting points during the DSC scans on the first heating. Only slight transitions with onset temperatures of 173 °C for F2BA, 202 °C for F3BA, and 181 °C for F4BA, were observed, which were attributed to glass transition temperatures ( $T_g$ 's). The high  $T_g$ 's of these materials suggest that the thermal treatment under mild conditions (110 °C, 2h, under vacuum) could be responsible for the production of thermally stable amorphous polymer networks. Second DSC heating scans, on both the cured and non-cured samples, however, no

longer exhibited any transitions below 250 °C. indicating that the dehydration was completed during the first heating scan and the resulting networks have an even higher crosslinking densities.

The TGA analysis of F2BA shows that this compound starts to lose weight as soon as heating commences with a rapid loss of weight occurring at 114 °C, due to the dehydration of boronic acid groups (Figure 3). The dehydration is almost complete once 150 °C has been reached with the weight remaining relatively constant up until 393 °C when the sample starts to decompose. Similar trends were observed for the other two samples F3BA and F4BA with a first transition (dehydration) at 72 and 82 °C, and a second transition (decomposition) at 427 and 426 °C, respectively. The weight losses due to the dehydration for F2BA, F3BA, and F4BA were 5.6%, 1.1%, and 2.3%, respectively. These values show some discrepancies with the calculated values (4.2%, 2.7%, and 2.2%, respectively), probably due to slight variations in the drying conditions used in their synthesis.



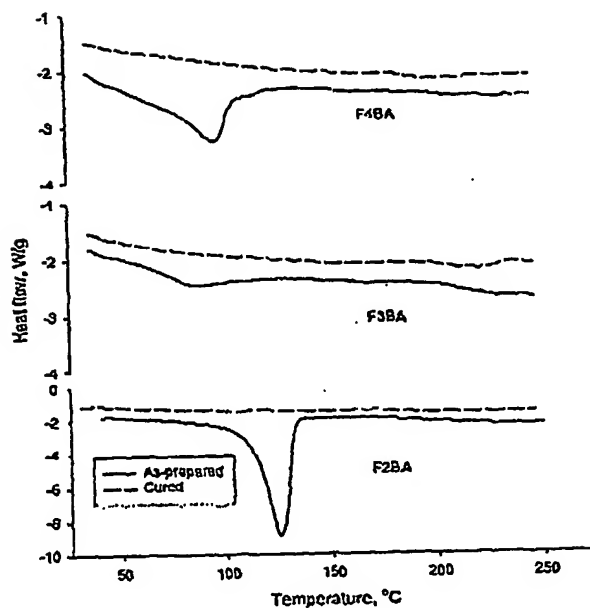


Figure 2. DSC curves (first heating run) of the oligofluorene diboronic acids at a heating rate of 10 °C/min under nitrogen (50 mL/min).

- 5 All three cured samples showed no weight losses prior to decomposition, indicating that complete dehydration of the samples had occurred under these chosen curing conditions (110 °C, 2h, under vacuum). The onset decomposition temperatures for the cured samples F2BA, F3BA, and F4BA were 405, 428, and 429 °C, respectively, very close to the results of the uncured samples (393, 427, and 426 °C). The 5% weight loss temperatures for the cured
- 10 F2BA, F3BA, and F4BA were 370, 417 and 420 °C, respectively. These results clearly demonstrate the high thermal stability of these crosslinked materials.

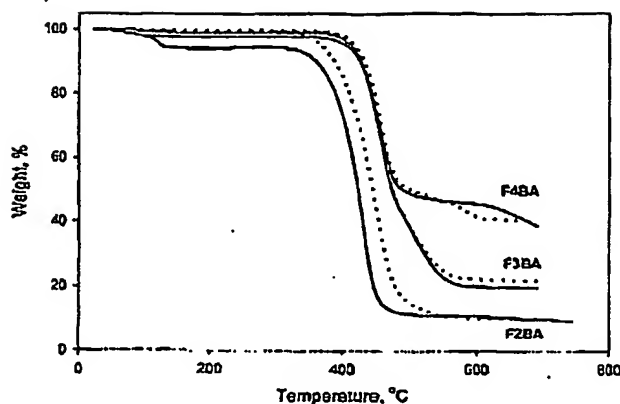


Figure 3. Weight loss curves for the as-prepared and cured F2BA, F3BA, and F4BA samples obtained at a heating rate of 5 °C/min under nitrogen (50 mL/min).

**Photophysical properties.** The UV-vis spectrum of F2BA in THF has a red-shifted, absorption maximum at 341 nm, compared with its precursor, dimers 3 ( $\lambda_{\text{max}}$  329 nm) and 4 ( $\lambda_{\text{max}}$  336 nm) (Figure 4 and Table 1). This red shift can be accounted for by the involvement of the boronic acid groups in the main chain conjugation. This arises because the B-O bond has been reported have some double bond character due to back coordination of the oxygen to boron. The samples F3BA and F4BA showed similar red-shifts in their  $\lambda_{\text{max}}$ 's (359 nm and 369 nm) compared with their corresponding oligomers 6 (352 nm), 7 (355 nm), 8 (363 m), and 9 (366). However, in these cases the contribution from the boronic acid groups appears to be less evident because of the increased length of the backbone. The photoluminescence spectrum of F2BA in THF exhibited two vibronic peaks at 376 and 397 nm, associated with a shoulder at 420 nm (Figure 4). Meanwhile F3BA has two emission peaks at 402 and 424 nm and a shoulder at 451 nm, while the F4BA displayed two peaks at 413 and 436 nm and a

shoulder at 465 nm. These peaks associated with F4BA are very close to those reported for polyfluorenes (415 and 439 nm). These oligofluorene diboronic acids are highly luminescent in solution with fluorescence yields ( $\Phi_f$ s) of 85% (F2BA), 96% (F3BA), and 98% (F4BA), respectively. These values are higher than those reported for most of polyfluorenes. The confinement of excitons in these conjugated oligofluorenes might explain their high fluorescence yields.

Table 1. Photophysical Properties of Oligofluorene diboronic acids.

	Solution			Films			
				As-prepared		After curing <sup>a</sup>	
	$\lambda_{\max, \text{abs}}$ nm	$\lambda_{\max, \text{em}}$ nm	$\Phi_f, \%$	$\lambda_{\max, \text{abs}}$ nm	$\lambda_{\max, \text{em}}$ nm	$\lambda_{\max, \text{abs}}$ nm	$\lambda_{\max, \text{em}}$ nm
<b>F2BA</b>	341	376, 397, 420(s)	85	341	387(sh) 406 429(sh)	349	392(s), 409, 433(s)
<b>F3BA</b>	359	402, 424, 451(s)	96	359	409, 429	363	411, 430
<b>F4BA</b>	369	413, 436, 465(s)	98	368	415, 438, 469(s)	369	416, 438, 473(s)

<sup>a</sup> Conditions: 60 °C under vacuum for 2h.

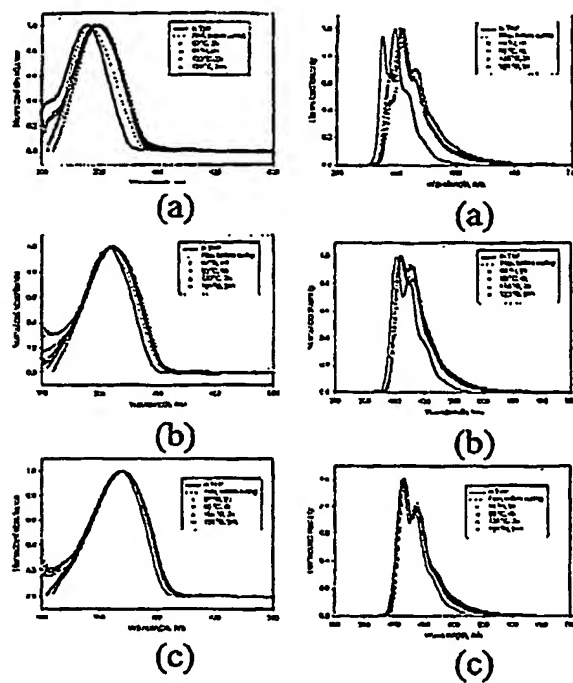


Figure 4. UV-vis (left) and photoluminescence spectra (right) of (a) F2BA, (b) F3BA, and (c) F4BA in solution and in the solid state.

Films of F2BA, F3BA, and F4BA were prepared by dissolving in THF (10 mg / mL THF), which contained a trace of water, drying over  $\text{MgSO}_4$ , and filtering. Spin-coating these solutions onto glass substrates gave uniform, transparent thin films, despite the fact that these compounds showed some extent of crystallinity in their powdery state. The as-spun films of F2BA, F3BA, and F4BA displayed absorption peaks at 341, 359, and 368 nm, respectively, nearly identical to those measured in solution (Figure 4 and Table 1). Under UV irradiation, F2BA films emitted violet-blue light, whereas films of F3BA and F4BA emitted bright blue light. Emission  $\lambda_{\text{max}}$ 's of these compounds bathochromically shifted 9 nm (from 397 to 406 nm) for F2BA, 7 nm (from 402 to 409 nm) for F3BA, and only 2 nm (from 413 to 415 nm)

for F4BA (Figure 4 and Table 1). The absence of any long wavelength emission peaks in the 500 – 600 nm region suggests that no aggregation was occurring in these thin films. The complete suppression of chain aggregation is likely attributable to the strong hydrogen bonding associated with the boronic acid groups that prevents the congregation of the oligomer

5 backbones. After being cured at 60 °C under vacuum for 2 h, the absorption  $\lambda_{\text{max}}$ 's of these films red-shifted 8 nm for F2BA, 4 nm for F3BA, and 1 nm for F4BA. Slight red-shifts in the emission  $\lambda_{\text{max}}$ 's were also observed for these films (3 nm for F2BA, 2 nm for F3BA, and 1 nm for F4BA). However, in all cases there were still no signs of long wavelength emissions and the red-shifts in the absorption and emission  $\lambda_{\text{max}}$ 's were assumed to be the result of the slight  
10 increase in conjugation due to the boxirine ring with the main chain  $\pi$ -system. Prolonged curing (60 °C, 4 h) or heating at a higher temperature (120 °C, 2 h) did not appear to cause any appreciable changes in the UV-vis and fluorescence spectra of these compounds indicating the absence of any chain aggregation and/or excimer formation. Even heating at 120 °C for 24 h caused no noticeable changes in the UV-vis spectrum of the F2BA film. Although the  
15 emission spectrum of the F2BA film showed a relatively lower emission peak at 392 nm and a more pronounced emission at 433 nm, the peaks were located at almost the same positions. These changes in the line shape of emission may be due to further formation of boroxines at elevated temperatures resulting in a slightly more extended conjugation system. The F3BA film after heating at 120 °C for 24 h also showed a very stable UV-vis spectrum. The emission  
20 peaks of the F3BA were also almost maintained at the same positions, even though the peak at 430 nm became slightly lower, probably due to the above-mentioned reason. On the other hand, there was almost no change in the UV-vis and fluorescence spectra of F4BA films after

being heating at 120 °C for 24 h. These results suggest that the amorphous architecture of the as-spun films were fully maintained in the cured films due to the transformation of the hydrogen bonding to the more stable boroxine linkages with the liberation of water molecules (Scheme 2). The fact that no long wavelength emission occurred in the 500 – 600 nm region were observed with any of these oligofluorene networks, clearly suggests that chain aggregation and/or excimer formation were fully suppressed.

**Part 2. Self-condensation of boronic acids to form amorphous polymer networks useful as hole-transporting materials**

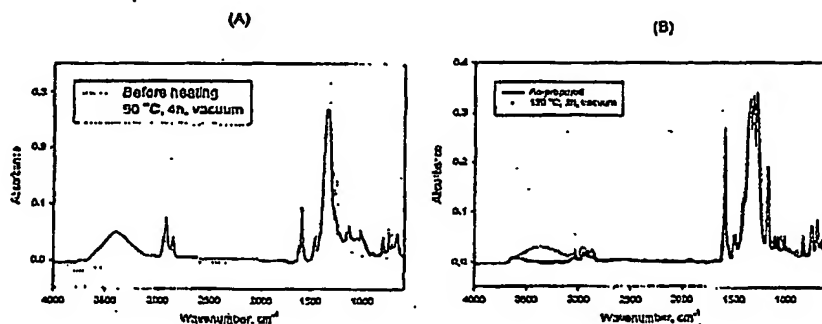
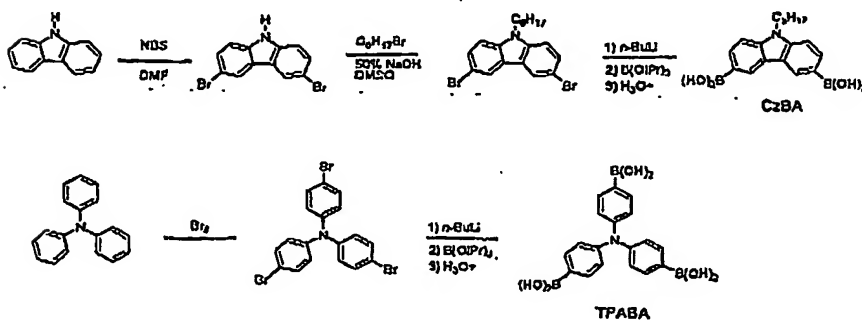


Figure 5. FT-IR spectra of as-prepared and cured films of (A) CzBA and (B) TPABA.

**Scheme 3. Synthesis of hole-transporting boronic acids.**



Carbazole and triarylamine derivatives are known good hole-transporting materials useful in LEDs. 9-Octylcarbazole-3,6-diboronic acid (CzBA) and tris(4-dihydroxyboranylphenyl)amine (TPABA) were synthesized (Scheme 3). Figure 5 clearly indicates the complete self-condensation of these materials after heating under vacuum at 90 °C/4 h for CzBA and 120 °C/2h for TPABA.

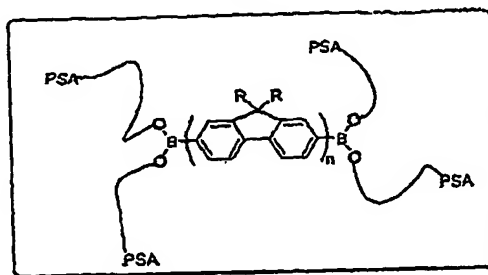
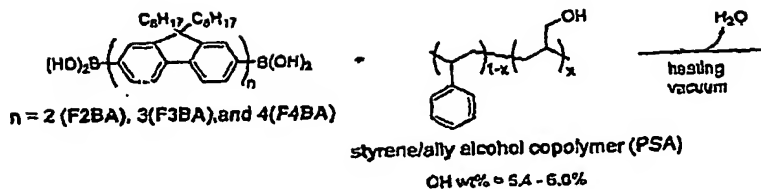
*Part 3. Esterification of boronic acids with polyols to form amorphous polymer networks useful as blue light emitting materials.*

1. Cross-linking reactions (Scheme 4).

F2BA, F3BA, and F4BA were dissolved in THF containing trace of water. Then PSA was dissolved in above solutions. The solutions were dried over MgSO<sub>4</sub> and were used to make films on KBr disks.

Scheme 4

20



cross-linked networks

After heating at 120 °C for 2h under vacuum, OH groups in boronic acids or polyols almost disappeared (Figure 6, 7, and 8), indicating the esterification is much more favored than the self-

5 condensation of boronic acids.

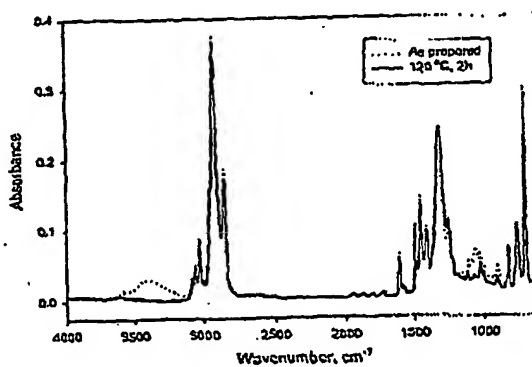


Figure 6. FT-IR spectra of F2BA/PSA samples.



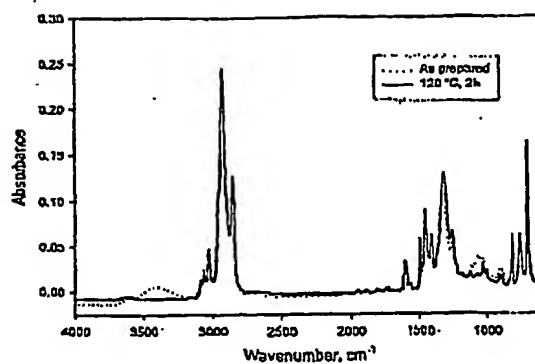
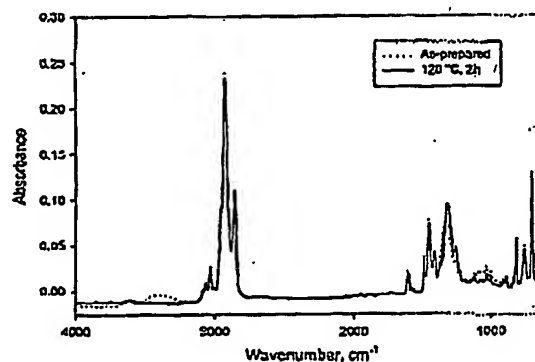


Figure 7. FT-IR spectra of F3BA/PSA samples.



5 Figure 8. FT-IR spectra of F4BA/PSA samples.

## 2. UV-vis and PL Properties.

UV-vis. Spectra. Thin films were fabricated on glass substrates from above solutions by spin-coating. The cross-linking was conducted in a vacuum oven at 120 °C for 2h. As shown in Table 2, the absorption maxima ( $\lambda_{\text{max}}$ 's) of the cured films exhibited slight blue shifts (2 nm), compared with as-prepared films, instead of red-shifts as observed for the cured films made by

10

self-condensation of boronic acids (F2BA, 341 to 349 nm; F3BA, 359 to 363 nm; F4BA, 368 to 369 nm).

Table 2. Photophysical properties of F<sub>n</sub>BA/PSA films.

Films	$\lambda_{\max}$ , UV-vis, nm			$\lambda_{\max}$ , Photoluminescence, nm		
	As-pre.	120 °C, 2h	120 °C, 24h	As-pre.	120 °C, 2h	120 °C, 24h
F2BA/PSA	340	338	338	383, 403	383, 403	381, 401
F3BA/PSA	356	354	354	406, 426	406, 426	405, 426
F4BA/PSA	366	364	364	413, 436	413, 436	413, 436

5

PL spectra (Figure 9, 10, and 11). The as-prepared films of F2BA/PSA, F3BA/PSA, and F4BA/PSA showed emission peaks (highest) at 403, 406, and 413 nm, respectively, which slightly red-shifted compared to those of the as-prepared films of F2BA (406 nm), F3BA (409 nm), and F4BA (415 nm). The cured films showed no any change in the emission peak positions and shapes within the instrumental error. On the other hand, the cured films of F2BA, F3BA, and F4BA red-shifted 3, 2, and 1 nm in their PL spectra, respectively. The intensity of the emission almost remains the same as the uncured samples, while the films made by self-condensation of F<sub>n</sub>BA showed reduced intensity after curing. The insulating PSA moieties worked better than the boroxine rings to trap or confine the excitons.

10

15

These samples show very thermally stable optical properties with almost no change in their UV-vis and PL spectra after heating at 120 °C for 24 h under vacuum. After heating in the air at 120 °C for 24 h, the UV-vis showed no appreciable changes. The shape of the PL spectra was maintained after heating in the air, but the intensity decrease about one third of the original

intensity. However no long wavelength emission was observed. These results indicate that oxidation occurs when these samples were exposed to air at elevated temperature, but the quenching effect is not as strong as observed in polymers with extended conjugation. The isolation of chromophores by insulating PSA might prevent the migration of excitons to the quenching sites generated by oxidation.

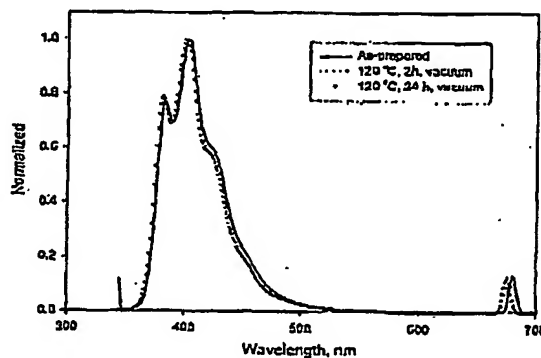


Figure 9. PL spectra of F2BA/PSA films.

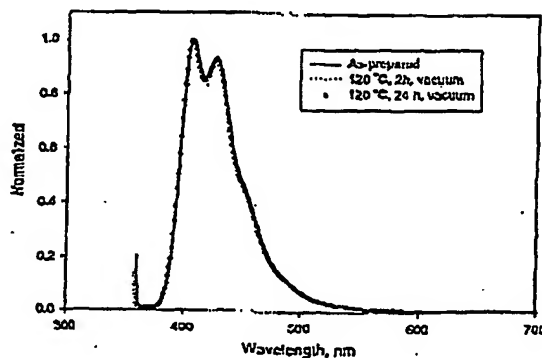


Figure 10. PL spectra of F3BA/PSA films.

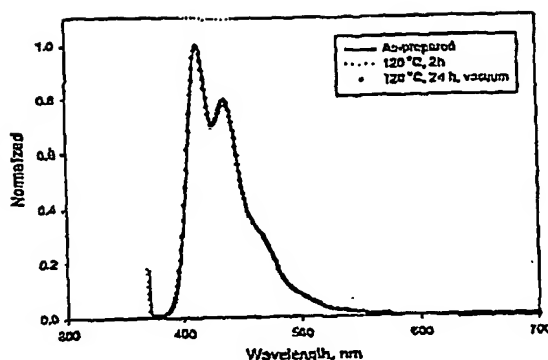


Figure 11. PL spectra of F4BA/PSA films.

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## 10 Conclusion

A novel approach based on the thermal dehydration of oligofluorene diboronic acids *via* the formation of boroxine linkages has been proposed to resolve the problems associated with chain aggregates and/or excimer formation that has often been observed polyfluorenes. The oligofluorene diboronic acids, F2BA, F3BA, and F4BA, were thus designed and synthesized. These compounds are readily soluble in organic solvents such as THF, acetone, and DMF. These compounds can be easily fabricated into uniform thin films by spin-coating from THF solutions onto glass substrates. These films can then be conveniently cross-linked using mild conditions (60 - 110 °C under vacuum for 2h) to form solvent-resistant and thermally stable

amorphous polymeric networks ( $T_g$ , 173 – 202 °C;  $T_d$  at 5% weight loss, 370 – 420 °C). The absorption and emission spectra of these thin films were also found to be thermally stable, showing no long wavelength emissions after being heated at 120 °C for 24 h. These stable blue light emitting materials would appear to be promising materials for organic emitters in LEDs.

- 5 The electroluminescence properties of these materials are currently under investigation. It also appears likely that this approach could be applied for hole- and electron-transporting materials in LEDs to stabilize their morphology and electro-optical properties. More importantly, since the crosslinked networks made by this method are insoluble in water alone and in anhydrous organic solvents, they allow the coating of succeeding layers to fabricate super-lattice structures and
- 10 multi-layered devices.

Arylamine derivatives CzBA and TPABA were synthesized. These boronic acids readily undergo self-condensation under mild conditions to form solvent-resistant polymeric networks. These materials are potentially applicable as hole-transporting materials in devices such as LEDs.

- 15 Esterification of boronic acids F2BA, F3BA, and F4BA with a commercially available polyol PSA were investigated. Esterification of boronic acid groups almost completes after heating at 120 °C for 2 h under vacuum. The crosslinked networks thus formed showed strong solvent-resistance. The spectral stabilities are also improved in respect with those prepared by thermal self-condensation of boronic acids alone, which are attributable to
- 20 the absence of weakly conjugated boroxine rings in these polymer networks.

## Appendix II

## 5 Fabrication and study of optical and electronic transport of the light emitting devices based on CzBA and F3BA

## 1. Fabrication of single- and double-layer thin films

Two types of materials containing boronic acid groups have been used for the preliminary study on the possibility of making a multi-layer structure: CzBA(hole transporting) and F<sub>3</sub>BA (electron-transporting, light emitting).

1. The CzBA thin films were spin-coated from a THF solution (20mg CzBA/ml), at 1500rpm for 50". The CzBA films prepared under this condition are about 110-120 nm thick. Films were heated in a vacuum oven at 130 °C for two hours to realize cross-link. No thickness change was found after the heat treatment (within 10% of accuracy). Small red shifts were found the UV-vis and fluorescence spectra, but the change in spectra is very small (Figure 1)

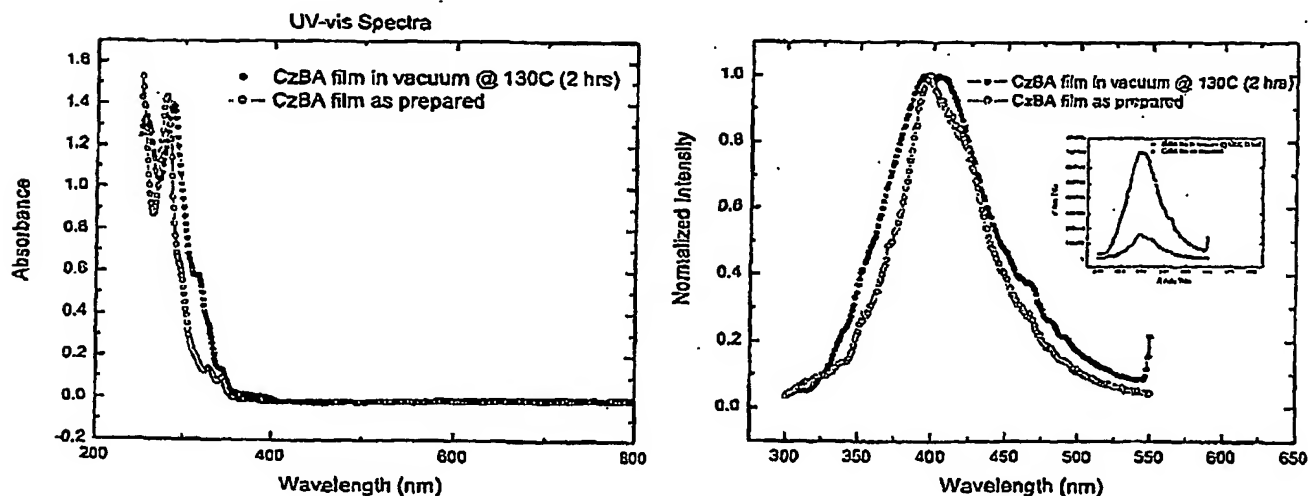


Figure 1

2. The F<sub>3</sub>BA thin films were spin-coated from a THF solution (20mg F<sub>3</sub>BA/ml), at 1500rpm for 50". The F<sub>3</sub>BA films prepared under this condition are about 120-130 nm

thick. Films were heated in a vacuum oven at 130 °C for two hours to realize cross-link. No thickness change was found after the heat treatment (within 10% of accuracy).

Small red shifts were found the UV-vis and fluorescence spectra. But the change in spectra is very small. One important feature in the FL spectra is that the intensity did not decrease after a thermal treatment in vacuum (Figure 2). An F<sub>3</sub>BA layer was also spin-cast on top of the CzBA thin film. The total thickness of the resulted double layer structure was 250 nm, that is the sum of the thickness of CzBA and F<sub>3</sub>BA layers.

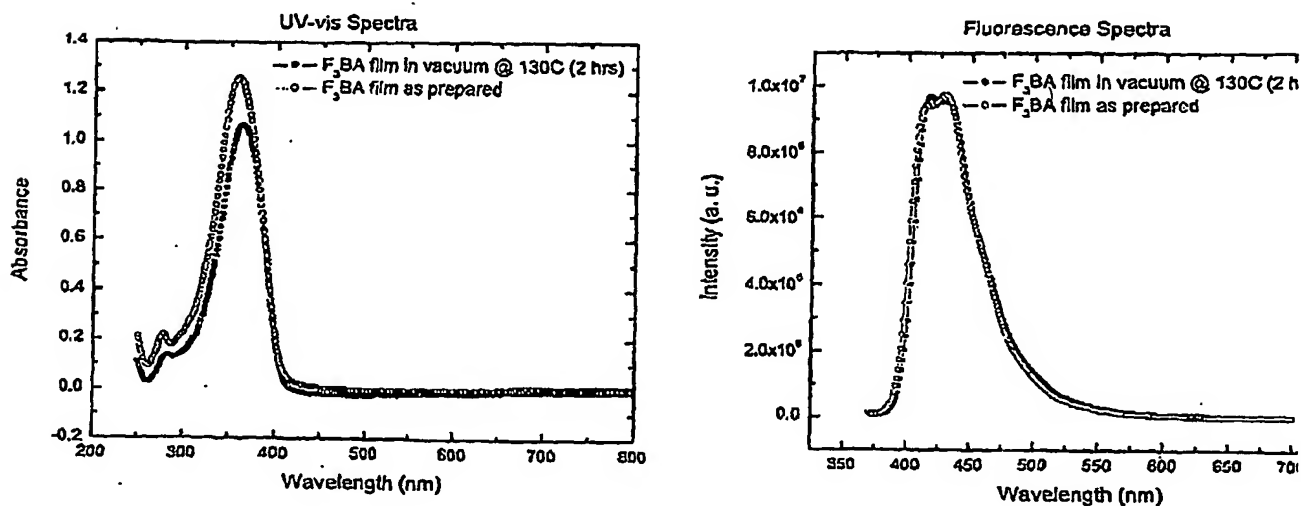
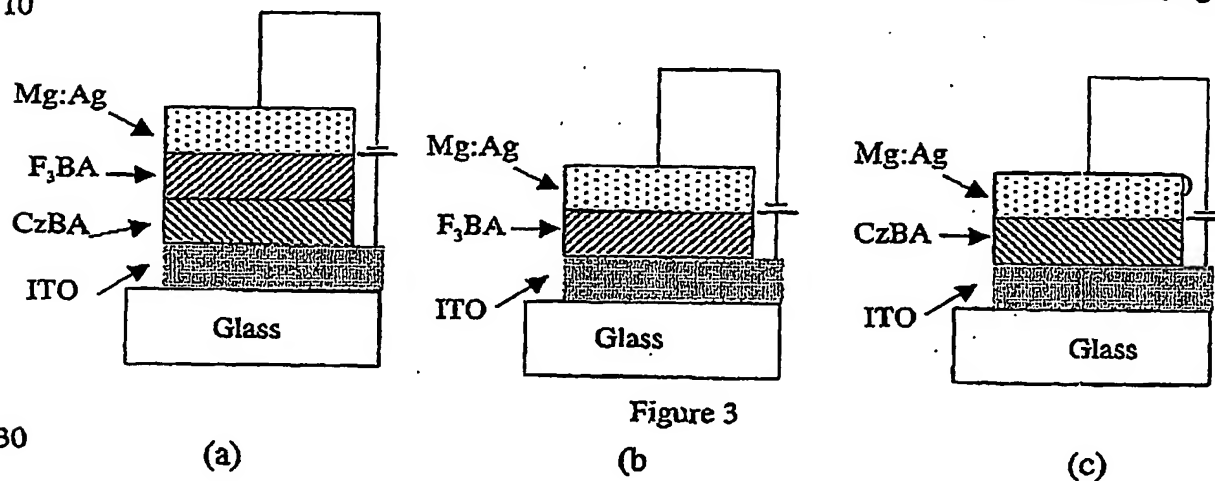


Figure 2

## Appendix III

# Fabrication and study of optical and electronic transport of organic light emitting devices based on CzBA and F<sub>3</sub>BA thin films:

ITO coated glass substrates were patterned using conventional photolithography and wet chemical etching. The pixel size is 5mm x 5mm. Thin films and double layer structure were prepared as described in Appendix I. Three device structures were used as follows (Figure 3):



Devices with double layer structure were successfully fabricated using CzBA and F<sub>3</sub>BA. CzBA layer functioned as a hole-transporting layer, and F<sub>3</sub>BA functioned as an emissive and electron-transporting layer. The following are the device performance data of OLEDs based on CzBA and F<sub>3</sub>BA double layer structure and F<sub>3</sub>BA single layer structure:

1. At the same electric field strength, the double layer structure device conducts much more electric current (current = hole current + electron current) (Figure 4).



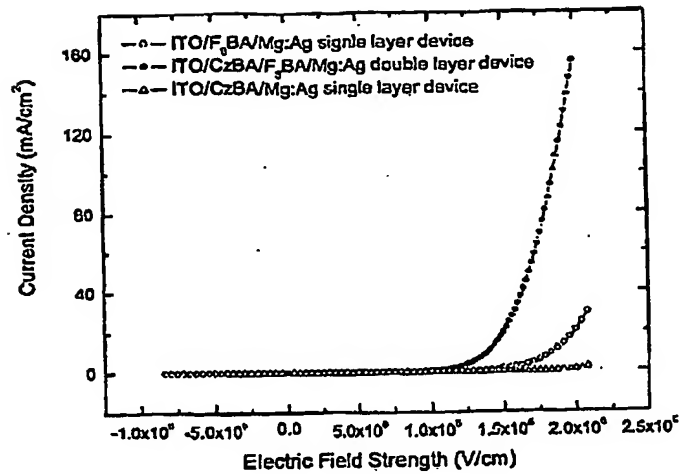


Figure 4

2. At the same electric field strength, the double layer structure device emits more light (Figure 5).

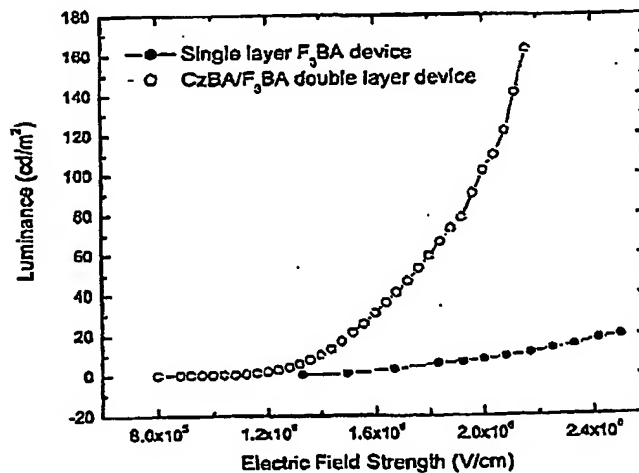


Figure 5

3. At the same electric current density, the double layer structure device emits more light, i. e. the device efficiency is much higher (Figure 6).

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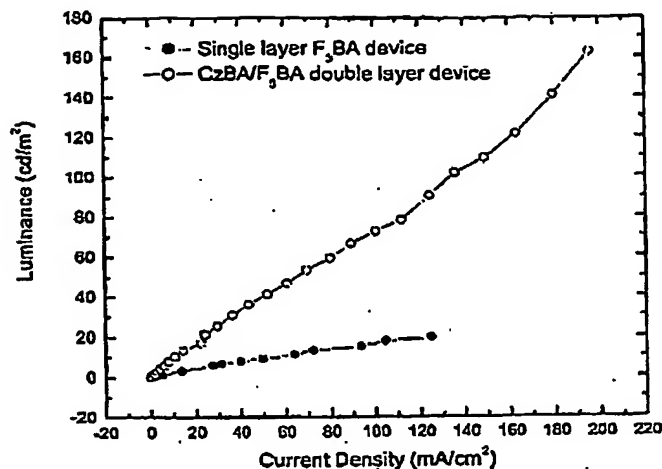


Figure 6

4. The electroluminescence spectrum of the CzBA/F<sub>3</sub>BA double layer device is identical to the photoluminescence spectrum of F<sub>3</sub>BA thin film (peaked @416nm). However, the EL spectrum of a single layer F<sub>3</sub>BA device is very different from the PL of F<sub>3</sub>BA thin film, there is a very broad long-wavelength shoulder beside the fluorene emission peak (Figure 7), that might be caused by imbalanced charge injection (electrons >> holes) in the device. In many cases, molecules are much less stable at charged state.

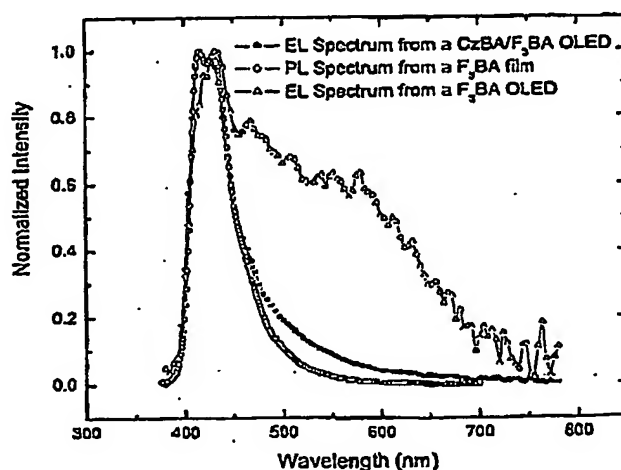


Figure 7

This series of experiments demonstrated that a double layer structure has been fabricated successfully using CzBA and F<sub>3</sub>BA. The hole-transporting layer and electron-transporting layer

functioned properly according to the design. That the fluorescence intensity did not decrease after a thermal treatment at 130 °C indicate the cross-link process is useful in enhancing the thermal stability, especially for fluorene-based compounds, which are know thermally unstable. The peak position of the EL emission at different driving voltages remained at 426 nm (Figure 8). This is a significant improvement as compared to other polyfluorene based LEDs.

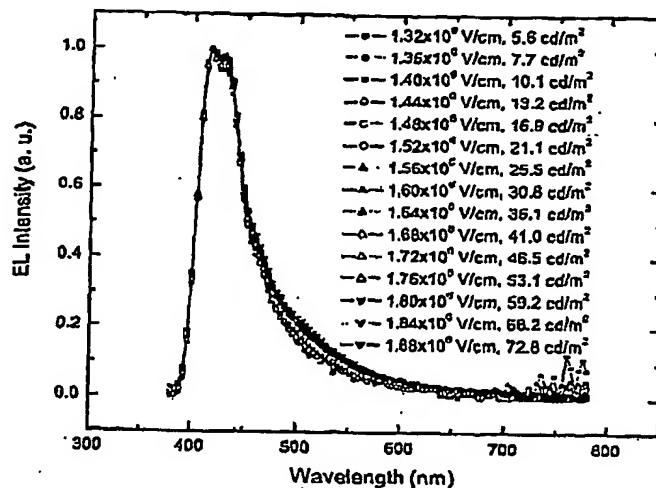


Figure 8

The maximum luminance value recorded for the CzBA/F3BA double layer device is around 170  $\text{cd/m}^2$ , this is because the luminance meter is calibrated as a photopic response device (Figure9).

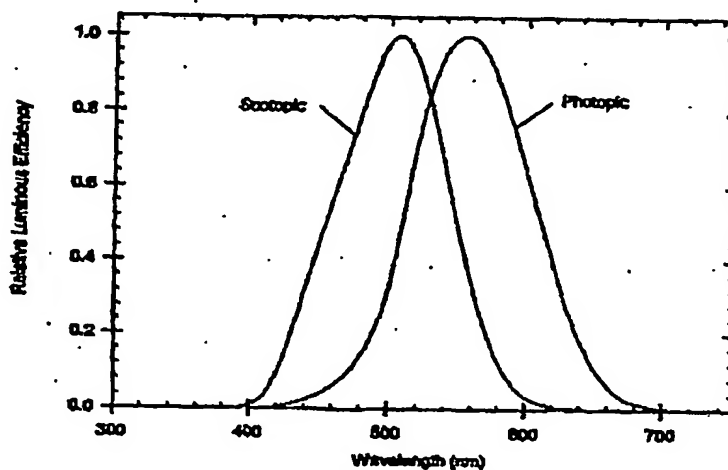


Figure 9 CIE spectral luminous efficiency functions for photopic vision,  $V(\lambda)$ , and scotopic vision,  $V'(\lambda)$ .

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